CLAIMS

[Claim(s)]

[Claim 1]A sputtering target for dielectric membrane formation, wherein an oxide which constitutes a target in a sputtering target for dielectric membrane formation is an oxide of an oxygen deficiency which decreased oxygen in the composing element and electrical resistivity is below 10ohm and m.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the sputtering target for dielectric membrane formation.

[0002]

[Description of the Prior Art]Many kinds of sputtering target for dielectric membrane formation are known from the former, Also in it, barium titanate [$BaTiO_3$], strontium titanate [$SrTiO_3$], The BST system of strontium titanate barium [(BaSr) TiO_3] which replaced some of them and barium [Ba] by strontium [Sr], or lead zirconate titanate [Pb(ZrTi) O_3], Material with a PLZT-PZT system of a lead-zirconate-titanate lantern [(PbLa) (ZrTi) O_3] which replaced a part of the lead [Pb] by the lantern [La] is used.

[0003]And the method of forming dielectric membrane forms membranes by a high frequency sputtering technique using said oxide dielectric (insulator) sintering target.

[0004]

[Problem(s) to be Solved by the Invention]The sputtering target for dielectric membrane formation is an insulator of an oxide, and by the direct-current sputtering technique, the forming-membranes method is not acquired but is performed by the high frequency sputtering technique.

[0005]When the composing element of a target is stable with not an oxide but metal, it is also possible to form membranes by a direct-current sputtering technique in the atmosphere which controlled the amount of oxygen using a metal target, but. For example, like metal strontium and metal barium, shortly after being exposed to the atmosphere in the case of a very activity metallic material, the surface is covered with an oxide film, and there is a problem that it cannot be used from the oxidation advancing further.

[0006]Although the forming-membranes method by a high frequency sputtering technique is an effective method to an insulator, as compared with a direct-current sputtering technique, ** high frequency current is required for it, and it is dramatically expensive as a sputtering system.

** In order to be stabilized and to make sputtering electric discharge perform, by a matching circuit, the impedance which changes with locating positions, such as an electrode in a device and a shutter, must be matched, and it becomes expensive complicated.

** During high frequency sputtering electric discharge, what is called reverse sputtering to which the spatter not only of the target of a cathode but the film formation substrate of an anode is carried out happens, and membrane formation speed is generally slow. There is a

problem to say.

[0007]On the other hand, generally in manufacturing an oxide sinter, it manufactures by an oxidizing atmosphere (including the inside of the atmosphere). However, it may manufacture by the inside of a vacuum, or a reducing atmosphere, and control of a crystal grain or density may be performed.

[0008]There was no idea of performing the sputtering target for membrane formation of the conventional oxide derivative thin film by a direct-current sputtering technique using the oxide target which, and introduced and low-resistance-ized the oxygen deficiency positively. [an oxide target] [use / oxide target] [membranes are formed by an exchange sputtering technique] [intend]

[0009]Therefore, an oxide target which is maintained by the stable discharge and which was low-resistance-ized was not obtained until now.

[0010]It aims at providing the sputtering target for dielectric membrane formation which this invention can cancel this problem and can use the stable direct-current sputtering technique.

[0011]

[Means for Solving the Problem]This invention persons completed this invention paying attention to introducing an oxygen deficiency and performing it by a direct-current sputtering technique using a low-resistance-ized oxide target positively, as a result of inquiring wholeheartedly.

[0012]When it states in detail, inside of the oxide material itself and those oxide materials, It is a thing [part / all of titanium dioxides [TiO_2] which are the oxides of titanium [Ti], or / its] using 3 oxidation 2 titanium [Ti_2O_3], titanium monoxide [TiO] or metallic titanium powder, etc., Those sintering processes are performed in a vacuum or a reducing atmosphere, and an oxygen deficiency is introduced positively.

[0013]When sintering a raw material which adjusted an oxide material or the 3 oxidation 2 aforementioned titanium, titanium monoxide, and titanium metal, an oxygen deficiency is positively introduced by covering all the circumferences or some of the raw material with titanium foil, and carrying out in a vacuum or a reducing atmosphere.

[0014]An oxide in which a sputtering target for dielectric membrane formation of this invention constitutes a target in a sputtering target for dielectric membrane formation is an oxide of an oxygen deficiency which decreased oxygen in the composing element, and it is characterized by electrical resistivity being 10 or less ohm-m.

[0015]

[Function]An oxygen deficiency is introduced positively and the stable direct-current spatter of the oxide dielectric target which has a very low electric resistance value becomes possible.

[0016]

[Example]The concrete example of this invention is described with a comparative example

below.

[0017]Example 1 -- the precursor powder end of strontium titanate barium [(BaSr) TiO_3] was prepared first.

[0018]Next, the die 3 made from graphite which has arranged the foil made from titanium [Ti] at each at the paries medialis orbitae 1 and the pars basilaris ossis occipitalis 2 which are shown in drawing 1, As shown in drawing 2, the bottom mold 4 made from graphite was first laid [the bottom mold 4 made from KURAFAITO] for the heating apparatus (not shown) in the vacuum housing 5 on the bottom hotpress 6 of the hotpresses 6 and 7 of one pair of built-in **** upper and lower sides, and the die 3 was laid on this bottom mold 4. The upper part hotpress 7 is raised in this case.

[0019]And after being filled up with 9 in the space part 8 of the die 3 in said end of precursor powder, in this end of precursor powder to the 9 up side. Titanium [Ti] Laying the foil 10 of make, laying the superior lamella 11 made from graphite from the upper part, dropping the **** [upper part / the] hotpress 7, and making between the up-and-down hotpresses 6 and 7 into the pressurization state of 300 - 400GPa. At the temperature of 1200-1500 **, the high vacuum hotpress of 1 hour was performed to the up-and-down hotpresses 6 and 7, and the disc-like sintered compact was produced with built-in **** heating apparatus to them. The degree of vacuum in the vacuum housing 1 in a high vacuum hotpress was set to 10^{-3}Pa.

[0020]The produced sintered compact was assuming a black color, the amount of oxygen in a sintered compact was [(BaSr) $TiO_{2.97}$], and electrical resistivity was $2x10^{-5}$ omega-m. The amount of oxygen was measured with X-ray diffraction and gravimetric measurement.

[0021]It was processed into disc-like spa TARRINGU target ST as shows drawing 3 the produced sintered compact, and 150-200-nm-thick dielectric membrane was formed on the substrate made from silicon by the direct-current sputtering technique using this sputtering target ST. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as oxygen and argon, and set impression direct current voltage to the target to 200V.

[0022]therefore, the oxide which constitutes a target being an oxide which has an oxygen deficiency, and electrical resistivity being 10 or less ohm-m, and the sputtering target of this example, When it used as a sputtering target, it was checked that membrane formation of dielectric membrane can be formed in the state where it was stabilized in the direct-current sputtering technique.

[0023]The degree of vacuum in an example 2 high-vacuum hotpress was set to 10^{-1} - 10^{-2}Pa, press pressure was set to 300 - 400GPa, sintering temperature was 1200-1500 **, and the sintered compact was produced by the same method as said Example 1 except having made sintering time into 1 hour. The produced sintered compact was assuming gray, the amount of

oxygen in a sintered compact was [(BaSr) $TiO_{2.99}$], and electrical resistivity was 1 ohm-m.

[0024]The produced sintered compact was processed into the sputtering target, and 150-200-nm-thick dielectric membrane was formed on the substrate made from silicon by the direct-current sputtering technique using this sputtering target. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as oxygen and argon, and set impression direct current voltage to the target to 200V.

[0025]therefore, the oxide which constitutes a target being an oxide which has an oxygen deficiency, and electrical resistivity being 10 or less ohm-m, and the sputtering target of this example, When it used as a sputtering target, it was checked that membrane formation of dielectric membrane can be formed in the state where it was stabilized in the direct-current sputtering technique.

[0026]The degree of vacuum in an example 3 high-vacuum hotpress was about 1 Pa, press pressure was set to 300 - 400GPa, sintering temperature was 1200-1500 **, and the sintered compact was produced by the same method as said Example 1 except having made sintering time into 1 hour. The produced sintered compact was assuming gray, the amount of oxygen in a sintered compact was [(BaSr) $TiO_{2.99}$], and electrical resistivity was 10 ohm-m.

[0027]The produced sintered compact was processed into the sputtering target, and 150-200-nm-thick dielectric membrane was formed on the substrate made from silicon by the direct-current sputtering technique using this sputtering target. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, atmosphere was used as oxygen and argon, and impression direct current voltage to the target was set to 200V.

[0028]therefore, the oxide which constitutes a target being an oxide which has an oxygen deficiency, and electrical resistivity being 10 or less ohm-m, and the sputtering target of this example, When it used as a sputtering target, it was checked that membrane formation of dielectric membrane can be formed in the state where it was stabilized in the direct-current sputtering technique.

[0029]Strontium titanate [$SrTiO_3$] is used as the precursor powder end of example 4 target,

The degree of vacuum in a high vacuum hotpress was set to 10^{-2} - 10^{-3}Pa, press pressure was set to 300 - 400GPa, sintering temperature was 1200-1500 **, and the sintered compact was produced by the same method as said Example 1 except having made sintering time into 1 hour. The produced sintered compact was assuming a black color, the amount of oxygen in a sintered compact was [$SrTiO_{2.97}$], and electrical resistivity was $2x10^{-4}$ omega-m.

[0030]The produced sintered compact was processed into the sputtering target, and 150-200-nm-thick dielectric membrane was formed on the substrate made from silicon by the direct-current sputtering technique using this sputtering target. The film formation condition in a

direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as oxygen and argon, and set impression direct current voltage to the target to 200V.

[0031]therefore, the oxide which constitutes a target being an oxide which has an oxygen deficiency, and electrical resistivity being 10 or less ohm-m, and the sputtering target of this example, When it used as a sputtering target, it was checked that membrane formation of dielectric membrane can be formed in the state where it was stabilized in the direct-current sputtering technique.

[0032]Strontium titanate [$SrTiO_3$] is used as the precursor powder end of example 5 target,

The degree of vacuum in a high vacuum hotpress was set to 10^{-1} - 10^{-2}Pa, press pressure was set to 300 - 400GPa, sintering temperature was 1200-1500 **, and the sintered compact was produced by the same method as said Example 1 except having made sintering time into 1 hour. The produced sintered compact was assuming gray, the amount of oxygen in a sintered compact was [$SrTiO_{2.98}$], and electrical resistivity was 2 ohm-m.

[0033]The produced sintered compact was processed into the sputtering target, and 150-200-nm-thick dielectric membrane was formed on the substrate made from silicon by the direct-current sputtering technique using this sputtering target. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as oxygen and argon, and set impression direct current voltage to the target to 200V.

[0034]therefore, the oxide which constitutes a target being an oxide which has an oxygen deficiency, and electrical resistivity being 10 or less ohm-m, and the sputtering target of this example, When it used as a sputtering target, it was checked that membrane formation of dielectric membrane can be formed in the state where it was stabilized in the direct-current sputtering technique.

[0035]Strontium titanate [$SrTiO_3$] is used as the precursor powder end of example 6 target,

The degree of vacuum in a high vacuum hotpress was set to 10^{-1} - 10^{-2}Pa, press pressure was set to 300 - 400GPa, sintering temperature was 1200-1500 **, and the sintered compact was produced by the same method as said Example 1 except having made sintering time into 1 hour. The produced sintered compact was assuming gray, the amount of oxygen in a sintered compact was [$SrTiO_{2.99}$], and electrical resistivity was 10 ohm-m.

[0036]The produced sintered compact was processed into the sputtering target, and 150-200-nm-thick dielectric membrane was formed on the substrate made from silicon by the direct-current sputtering technique using this sputtering target. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as oxygen and argon, and set impression direct current voltage to the target to 200V.

[0037]therefore, the oxide which constitutes a target being an oxide which has an oxygen

deficiency, and electrical resistivity being 10 or less ohm-m, and the sputtering target of this example, When it used as a sputtering target, it was checked that membrane formation of dielectric membrane can be formed in the state where it was stabilized in the direct-current sputtering technique.

[0038]Using the precursor powder end of the same strontium titanate barium [(BaSr) TiO_3] as the comparative example 1 aforementioned example 1, this was sintered at the temperature of 1200-1500 ** in the atmosphere after fabricating to disc-like with the conventional method, and the comparative example sintered compact was produced. The produced comparative example sintered compact was assuming white, the amount of oxygen in this sintered compact was [(BaSr) TiO_3], and electrical resistivity was more than $1x10^{10}$ omega-m.

[0039]This comparative example sintered compact was processed into the sputtering target, using this sputtering target, it carried out in order to form dielectric membrane on the substrate made from silicon by a direct-current sputtering technique, but DC sputtering was not able to be performed. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as argon, and set impression direct current voltage to the target to 200V.

[0040]Therefore, the membrane formation of the dielectric membrane by a direct-current sputtering technique was not able to perform the sputtering target (there is no oxygen deficiency) of the comparative example.

[0041]Using the precursor powder end of the same strontium titanate [$SrTiO_3$] as the comparative example 2 aforementioned example 6, this was sintered at the temperature of 1200-1500 ** in the atmosphere after fabricating to disc-like with the conventional method, and the comparative example sintered compact was produced. The produced comparative example sintered compact was assuming white, the amount of oxygen in this sintered compact was [$SrTiO_3$], and electrical resistivity was more than $1x10^{10}$ omega-m.

[0042]This comparative example sintered compact was processed into the sputtering target, using this sputtering target, it carried out in order to form dielectric membrane on the substrate made from silicon by a direct-current sputtering technique, but DC sputtering was not able to be performed. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as argon, and set impression direct current voltage to the target to 200V.

[0043]Therefore, the membrane formation of the dielectric membrane by a direct-current sputtering technique was not able to perform the sputtering target (there is no oxygen deficiency) of the comparative example.

[0044]As the precursor powder end of comparative example 3 lead zirconate titanate [Pb(ZrTi)

O_3], Lead oxide [PbO], zirconium oxide [ZrO_2], and a titanium dioxide [TiO_2] were prepared, and it mixed by the predetermined ratio, and it molded and pressed with the conventional method, sintered at the temperature of 1200-1500 ** in the atmosphere after fabricating to disc-like, and the comparative example sintered compact was produced.

[0045]The produced comparative example sintered compact was assuming white, the amount of oxygen in this sintered compact was [Pb(ZrTi) O_3], and electrical resistivity was more than $1x10^{10}$ omega-cm.

[0046]This comparative example sintered compact was processed into the sputtering target, using this sputtering target, it carried out in order to form dielectric membrane on the substrate made from silicon by a direct-current sputtering technique, but DC sputtering was not able to be performed. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as argon, and set impression direct current voltage to the target to 200V.

[0047]Therefore, the membrane formation of the dielectric membrane by a direct-current sputtering technique was not able to perform the sputtering target (there is no oxygen deficiency) of the comparative example.

[0048]Example 7 -- first, as the precursor powder end of lead zirconate titanate [Pb(ZrTi) O_3], lead oxide [PbO] zirconium oxide [ZrO_2] 3 oxidation 2 titanium [Ti_2O_3] was mixed by the predetermined ratio, and the end of precursor powder was prepared.

[0049]Next, the die 3 made from graphite which has arranged the foil made from titanium [Ti] at each at the paries medialis orbitae 1 and the pars basilaris ossis occipitalis 2 which are shown in drawing 1, As shown in drawing 2, the bottom mold 4 made from graphite was first laid [the bottom mold 4 made from graphite] for the heating apparatus (not shown) in the vacuum housing 5 on the bottom hotpress 6 of the hotpresses 6 and 7 of one pair of built-in **** upper and lower sides, and the die 3 was laid on this bottom mold 4. The upper part hotpress 6 is raised in this case.

[0050]And after being filled up with 9 in the space part 8 of the die 3 in said end of precursor powder, in this end of precursor powder to the 9 up side. Titanium [Ti] Laying the foil 10 of make, laying the superior lamella 11 made from graphite from the upper part, dropping the **** [upper part / the] hotpress 7, and making between the up-and-down hotpresses 6 and 7 into the pressurization state of 300 - 400GPa. At the temperature of about 800 **, the high vacuum hotpress of 0.5 hour was performed to the up-and-down hotpresses 6 and 7, and the disc-like sintered compact was produced with built-in **** heating apparatus to them. The degree of vacuum in the vacuum housing 1 in a high vacuum hotpress was set to about 10^{-1}Pa.

[0051]3 oxidation 2 titanium [Ti_2O_3] of the raw material should replace the quantity equivalent

to titanium [Ti] in the titanium dioxide [TiO_2] of said comparative example 3 by 3 oxidation 2 titanium [Ti_2O_3].

[0052]The produced sintered compact was assuming a black color, the amount of oxygen in a sintered compact was [$Pb(ZrTi)O_{2\cdot98}$], and electrical resistivity was $5x10^{-3}$ omega-m.

[0053]It was processed into disc-like spa TARRINGU target ST as shows drawing 3 the produced sintered compact, and 150-200-nm-thick dielectric membrane was formed on the substrate made from silicon by the direct-current sputtering technique using this sputtering target ST. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as oxygen and argon, and set impression direct current voltage to the target to 200V.

[0054]therefore, the oxide which constitutes a target being an oxide which has an oxygen deficiency, and electrical resistivity being 10 or less ohm-m, and the sputtering target of this example, When it was considered as a sputtering target and used, it was checked that membrane formation of dielectric membrane can be formed in the state where it was stabilized in the direct-current sputtering technique.

[0055]The degree of vacuum in an example 8 high-vacuum hotpress was set to 1 - 10^{-1}Pa, press pressure was set to 300 - 400GPa, sintering temperature was about 800 **, and the sintered compact was produced by the same method as said Example 7 except having made sintering time into 0.5 hour.

[0056]The produced sintered compact was assuming gray, the amount of oxygen in a sintered compact was [$Pb(ZrTi)O_{2\cdot99}$], and electrical resistivity was 10 ohm-m.

[0057]The produced sintered compact was processed into the sputtering target, and 150-200-nm-thick dielectric membrane was formed on the substrate made from silicon by the direct-current sputtering technique using this sputtering target. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as oxygen and argon, and set impression direct current voltage to the target to 200V.

[0058]therefore, the oxide which constitutes a target being an oxide which has an oxygen deficiency, and electrical resistivity being 10 or less ohm-m, and the sputtering target of this example, When it used as a sputtering target, it was checked that membrane formation of dielectric membrane can be formed in the state where it was stabilized in the direct-current sputtering technique.

[0059]The degree of vacuum in an example 9 high-vacuum hotpress was set to 1 - 10^{-1}Pa, press pressure was set to 300 - 400GPa, sintering temperature was about 800 **, and the sintered compact was produced by the same method as said Example 7 except having made sintering time into 0.5 hour.

[0060]The produced sintered compact was assuming gray, the amount of oxygen in a sintered compact was [Pb(ZrTi) $O_{2.99}$], and electrical resistivity was 1 ohm-m.

[0061]The produced sintered compact was processed into the sputtering target, and 150-200-nm-thick dielectric membrane was formed on the substrate made from silicon by the direct-current sputtering technique using this sputtering target ST. The film formation condition in a direct-current sputtering technique was 5x10 Pa in degree of vacuum, used atmosphere as oxygen and argon, and set impression direct current voltage to the target to 200V.

[0062]therefore, the oxide which constitutes a target being an oxide which has an oxygen deficiency, and electrical resistivity being 10 or less ohm-m, and the sputtering target of this example, When it used as a sputtering target, it was checked that membrane formation of dielectric membrane can be formed in the state where it was stabilized in the direct-current sputtering technique.

[0063]Although titanium was used for the die 3 made from graphite used when obtaining a target (sintered compact) as an arrangement **** metallic foil in said each example, In this invention, when performing sputtering at the target instead of what is limited to this and forming dielectric membrane, the foil of metal [activity / hafnium / a zirconium [Zr], / [Hf]] may be used in the range without the influence on membrane formation.

[0064]Although 3 oxidation 2 titanium [Ti_2O_3] powder was used as one of the raw materials of lead zirconate titanate in said Example 7, Instead of 3 oxidation 2 titanium [Ti_2O_3] powder instead of what is limited to this in this invention, 5 oxidation 3 titanium [Ti_3O_5] powder, Or the mixture of titanium metal [Ti] powder or 3 oxidation 2 titanium [Ti_2O_3] 5 oxidation 3 titanium [Ti_3O_5] and titanium metal [Ti] may be used, and the quantity is good also as the whole quantity in part.

[0065]If the electrical resistivity of a sputtering target is 10 or less ohm-m, membrane formation of the dielectric membrane by a direct-current sputtering technique is possible, but in order to make sputtering perform by the stable discharge, below 10^{-1} omega-m is desirable.

[0066]

[Effect of the Invention]Thus, since the oxide in which a sputtering target constitutes a target is an oxide of an oxygen deficiency and electrical resistivity is 10 or less ohm-m, when based on this invention, Since the dielectric membrane which was obtained only by the high frequency sputtering technique and which was not can be conventionally formed by a direct-current sputtering technique, Since a cheap DC-sputtering device can be used and membrane formation speed can be brought forward as compared with a high frequency sputtering technique, it has the effect that the high sputtering target of mass production nature can be provided by low cost.

[Translation done.]